Grain boundary effect on charge transport in pentacene thin films

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1. Introduction

Semiconductor devices using organic materials [1], such as thin film transistors [2] and light emitting diodes [3] have attracted a lot of research interests. Although the mobility (as a main parameter required for applications) is comparable with amorphous hydrogenated silicon, fabrication of the high mobility devices is still difficult. Hence, study of the charge propagation through the organic devices is one of main challenges of present applied physics. In contrast to inorganic semiconductors organic materials have different mechanical, optical and partially also electrical properties.

In contrast to the inorganic semiconductors, it was not possible to prepare organic semiconductors in single-crystal form for many years. Therefore, low mobility of organic materials was associated with the material crystallinity. Increase of the grain size was widely studied and related to the rise of mobility [4]. Hence, the single-crystal was the final goal of organic semiconductor technology and it was successfully reached for rubrene [5]. Surprisingly, the carrier mobility was comparable with other polycrystalline materials, like pentacene [6].

On the other hand, localized levels created between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are assigned to the charge trapping phenomenon. It was reported that the origin of these levels dwells in imperfections of the crystal structure or in the chemical modification of organic semiconductor molecules [7,8]. The former one is related to the crystal size, while the later one represents e.g. oxidation, which is common for organic materials.

In this work we present study of charge transport in pentacene thin films of different crystallinity and its relation to the oxygen-related defect, i.e., pentacenequinone. Pentacene crystal size is controlled by the evaporation rate without distortion of the in-grain order. We illustrate decrease of the organic material conductivity with crystal size reduction as well as with a significant rise of the pentacenequinone concentration in the pentacene thin film. We show that the organic semiconductor crystal size influences oxygen diffusion in thin films.

2. Experiment

Top-contact pentacene organic field-effect transistors (OFETs) were used in the present experiments. The heavily-doped Si wafers with a 100 nm thick thermally prepared silicon dioxide (SiO_2) insulating layer were used as the base substrates for OFET structures. During the deposition of pentacene ($C_{22}H_{14}$), the pressure was kept at less than 10^{-4} Pa and the evaporation rate was fixed in the range from 0.5 to 10 Å/s, monitored by using a quartz crystal microbalance. Under these conditions 100 nm thick pentacene films were deposited.

Thereafter, source and drain gold electrodes with a thickness of 50 nm were deposited on the pentacene surface. The designed channel length (L) and width (W) of OFETs were 50 μm and 3 mm, respectively. Prepared devices were characterized by the standard steady-state current-voltage measurement using Keithley 2400 SourceMeter. The surface topography and roughness analysis was done with the atomic force microscopy (high-resolution AFM microscope Solver P47-PRO) on 300 nm thick films deposited on the SiO_2 surface. Steady-state voltammograms (anodic scans, i.e., the hole capture in deep traps is measured [9]) with the scan rate of 3.33 mV/s were obtained in a three-electrode electrochemical cell equipped with an Ag/AgCl reference electrode and a Pt counter electrode. The working electrode consisted of a round gold sheet (of 1.5 mm in the diameter) covered with pentacene thin film. In case of steady-state conditions these signals have voltammetric wave at the redox potential. All the chemicals used were of analytical grade, solutions were prepared in bidistilled water.
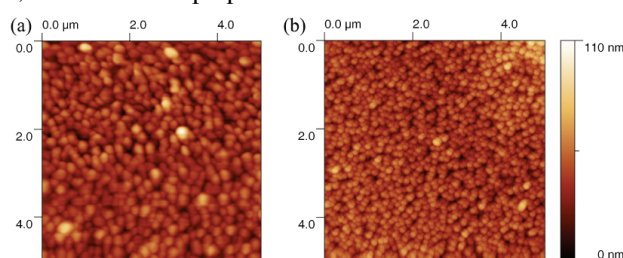

Fig. 1 AFM topography of pentacene film surface for evaporation rate of (a) 0.5 and (b) 10 Å/s.

3. Results and Discussion

The thermal evaporation provides us polycrystalline pentacene thin films with a crystal size dependent on the evaporation rate. Figure 1 depicts typical image of pentacene topography for two evaporation rates of 0.5 and 10 Å/s. Although the samples with slow and fast evaporated pentacene films have the mean crystal size of 0.3 and 0.1

⊤m, respectively, the mean surface roughness of 10 nm is conserved. Note that for all evaporation rates used no difference in the x-ray diffraction pattern has been observed. Hence, we can use various evaporation rates to prepare various grain sizes without distortion of the in-grain order.

The effect of grain size on the charge transport was investigated with the OFET devices. Here, the transport phenomenon is sensitive to the internal field, which influences opening of the OFET channel represented by the threshold voltage V_{th}. In contrast to two-electrode metal–organic semiconductor film–metal structures, the charge is transported on the organic semiconductor–gate insulator interface. Transfer characteristics of OFETs with 0.5 and 10 Å/s evaporated pentacene films are shown in Fig. 2.
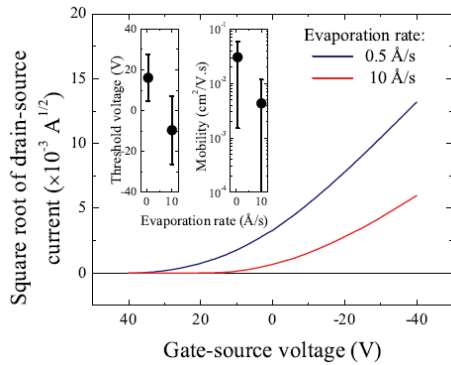

Fig. 2 Transfer characteristics of OFET for pentacene evaporation rate of 0.5 and 10 Å/s. Inset illustrates average threshold voltages and average mobilities obtained for various samples.

In addition, obvious shift of the threshold voltage from +10 to -1 V is observed. This shift is assigned to the presence of additional trapped charges Q_t at the pentacene–gate insulator interface. The charges trapped in pentacene film influence the local electric field and therefore after compensation of this additional field the carrier transport is possible. This effect can be evaluated by the threshold voltage shift ΔV_{th} by relation

$$Q_t = C_g \Delta V_{th} \qquad (1)$$

where C_g is the gate insulator capacitance per unit of area. Since output characteristics of both slow and fast evaporated pentacene OFET show discrepancy in the threshold voltage of 11 V, the trapped charge density can be estimated as $9 \times 10^{10}/cm^2$.

This result is interesting to compare with steady-state voltammetry experiment, which can identify kind of chemical defect, e.g. pentacenequinone ($C_{22}H_{14}O$, PQ). The steady-state voltammetry analysis was done for both 0.5 and 10 Å/s evaporated films and for various solutions prepared as follows. Hydrochloric acid and/or natrium hydroxide were added into the bidistilled water to obtain various pH. For fast evaporation rates a significant increase of

the defect density is obvious. Detail defect evolution is plotted in Fig. 3, where the derivative voltammetric signal is used for the concentration changes estimation.
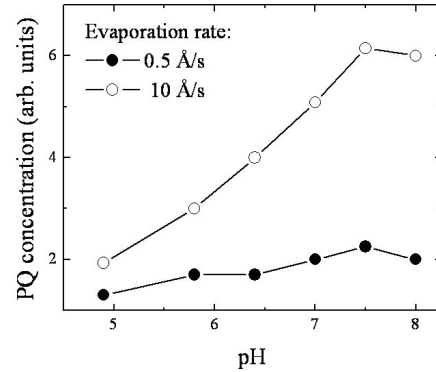

Fig. 3 Pentacene defects concentrations vs. pH of the solution.

We can conclude that fast evaporated films are more sensitive to the gaseous as well as wet environment. Here should be noted that experiments were done in steady state, thus the difference in the defect concentration due to the diffusion process can be neglected. Therefore, the increase of the defect concentration is related to the rise of the binding sites in pentacene films due to smaller grain size (*i.e.*, faster evaporation).

Conclusions

As an interpretation of obtained data we suggest accumulation of defects on the grain boundary. The increase of the PQ defect density by factor of 3 (for the fast evaporation rate) roughly corresponds to the increase of the grain boundary, where the average grain diameter decreased also by factor of 3 from 0.3 to 0.1 μm.

References
[1] H. E. Katz, J. Mater. Chem. **7** (1997) 369.
[2] H. Sirringhaus, Adv. Mater. **17** (2005) 2411.
[3] C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. **51** (1987) 913.
[4] C. Kim, A. Facchetti, T. J. Marks, Science, **318** (2007) 76.
[5] V. Podzorov, V.M. Pudalov, and M.E. Gershenson, Appl. Phys. Lett., **82** (2003) 1739.
[6] C.D. Dimitrakopoulos, S. Purushothaman, J. Kymissis, A. Callegari, and J.M. Shaw, Science **283** (1999) 822.
[7] J.E. Northrup and M.L. Chabinyc, Phys. Rev. B **68** (2003) 041202.
[8] V. Nádaždy, R. Durný, J. Puigdollers, C. Voz, S. Cheylan, M. Weis, J. Non-Cryst. Solids **354** (2008) 2888.
[9] K. Gmucová, M. Weis, M.D. Pirriera, and J. Puigdollers, Phys. Stat. Sol. (a) **206** (2009) 1404.